N91-28085

S22-25
26603
p.5

THE FORMATION AND STUDY OF TITANIUM, ZIRCONIUM AND HAFNIUM COMPLEXES

Bobby Wilson, Sam Sarin, Laverne Smith and Melanie Wilson
Department of Chemistry
Texas Southern University
3100 Cleburne
Houston, Texas

ABSTRACT

Research involves the preparation and characterization of a series of Ti, Zr, Hf, TiO, and HfO, complexes using the poly(pyrazolyl)borates as ligands. The study will provide increased understanding of the decomposition of these coordination compounds which may lead to the production of molecular oxygen on the moon from lunar materials such as ilmenite and rutile. These model compounds are investigated under reducing conditions of molecular hydrogen by use of a high temperature/pressure stainless steel autoclave reactor and by thermogravimetric analysis.

Introduction

Currently, there is considerable interest in the United States in producing molecular oxygen from lunar ores to be used as fuel and in life support systems for space travel. Ilmenite ($FeTiO_3$) and rutile (TiO_2) are both abundant on the moon. Reduction of these ores to produce the pure metal and molecular oxygen is most desirable. Even though several technically different approaches are reported in the literature, none is acceptable for use on the moon.

A survey of the literature on research concerning the use of ilmenite and rutile in the generation of O_2 and Ti brings us to the following conclusions: (1) There is evidence of a lack of research in the above stated direction because of the focus of many industrial firms is the extraction and use of pure TiO_2 and Ti in other processes with no attention being given to the recyclability and energy efficiency of oxygen production(1). However, on the positive side, a variety of these processes do appear to be adaptable to lunar processing, with the modification of these chemical processes. The real bonus of lunar processing is the inert atmosphere, which is very conducive for the production of ultra pure titanium. Because of the considerable amount of energy and time wasted in the earth processes to effect high temperature vacuum annealing of titanium, reduction in a lunar environment becomes even more attractive (2). For example, the Plasma Reduction Process which occurs at 25000 to 35000 K with hydrogen is clean when there are no leaks from the environment (3). The reactions may be written as follows:

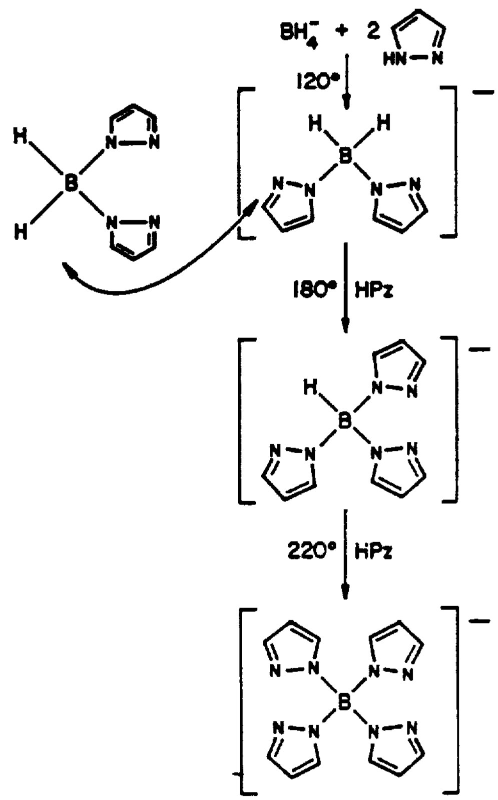
$$TiO_2 + 2H_2 \; ----> \; Ti + 2H_2O$$

$$2H_2O \; ----> \; 2H_2 + O_2$$

One solution to the improvement of the TiO_2 reduction is the development of appropriate catalysts that will enhance a lunar process. These catalysts must be chemically stable, or be converted into species which are stable under the conditions required to reduce TiO_2 or $FeTiO_3$ to Fe, Ti and O_2 which may be quite severe. The primary purpose of this research is to prepare and characterize a series of Ti, Zr, Hf, TiO and HfO complexes using the poly(pyrazolyl) borates as ligands.

The poly(pyrazolyl)borates, anions of the general structure $(H_nB\,(Pz)_{4-n})^-$, (where n=0,1 or 2) can be made to function as a bidentate ligand, a tridentate ligand of C_{3v} symmetry analogous to the cyclopentadienide anions, and even as a tetradentate (bis-bidentate) ligand with appropriate control substituents (see Scheme 1 (4-7)). The formation of transition metal complexes with these ligands allows for the option of varying the form (group attachment) of the ligand that is used in the preparation of the coordination complex. The aim is to determine the importance of altering the molecular weight and size of the poly(pyrazolyl)borate and to correlate the chelate effect on complex formation. The decomposition temperature of the enclosed metal complex should have a profound effect upon the metallurgical aspects of the lunar material. Thermogravimetric analyses are currently under study on selected samples under an inert atmosphere in an effort to correlate decomposition temperature with speciation.

SCHEME I



Experimental Details

Since the compounds synthesized during this study were sensitive to air and moisture, all syntheses and subsequent handling of the compounds were conducted under vacuum or in an inert atmosphere. Samples and solutions were prepared in a nitrogen-filled glove box.

Materials

Titanium tetrabromide and titanium tetraiodide (97%), obtained from Alfa Inorganic Products, were used as received. Potassium borohydride (98%) and pyrazole, which were obtained from Fisher Scientific, were also used as received. Analytical grade methylene chloride was purchased from Fisher Scientific Company and dried by refluxing for 24 hours over calcium hydride.

Preparation

Ligand - the following reaction gives rise to potassium dihydrobis(pyrazolyl)borate, $K(H_2B(Pz)_2)$:

$$KBH_4 + 2HPz \text{ ----> } K(H_2B(Pz)_2) + 2H_2$$

The potassium dihydrobis(pyrazolyl)borate was prepared by mixing potassium borohydride (45 g, 1 mole) with pyrazole (272 g, 4 moles) in a one-liter round bottom flask equipped with a magnetic stirrer, thermometer and vent line. The pyrazole was carefully melted by means of an oil bath at 90°C. When the contents of the flask were sufficiently molten to allow magnetic stirring, the mixture was stirred and heated to 120°C. Potassium borohydride dissolved slowly with the evolution of hydrogen. After 24 hours, only a few small particles of KBH_4 were still floating in the melt. These particles were removed mechanically. The melt was poured into 500 ml of toluene, stirred until it cooled to room temperature, and filtered. The filter cake was washed three times with 150 ml portions of hot toluene and then air dried, yielding 140 g of white solid with a melting point of range of 171 - 172°C (8).

Metal Complexes

Preliminary results are consistent with the following reactions on preparation of the titanium complexes:

$$TiX_4 + 2K[H_2B(Pz)_2] \text{ ----> } TiX_2[H_2B(Pz)_2]_2 + 2KX$$

$$TiX_4 + 4K[H_2B(Pz)_2] \text{ ----> } Ti[H_2B(Pz)_2]_4 + 4K$$

(where X = Br and I)

Results and Discussion

Compounds of early transition metals in oxidation state IV are extremely sensitive to oxygen and/or moisture. Therefore, it is essential that all manipulations of these complexes be effected under inert conditions. Since these compounds require special working conditions, relatively few have been prepared and fully characterized. We feel that the poly(pyrazolyl)borate anions with their good chelating abilities and uni-negative property afford an excellent opportunity to increase our knowledge in this area of inorganic chemistry. It is known that the choice of ligands influences the stereochemistry of the metal ions. Small donors decrease the steric repulsions and tend to favor the higher coordination numbers. Large donors tend to favor lower coordination because of the increase in steric repulsions. This series of ligands allows us to test both trends without changing the donor atoms or charge on the ligand. It is also known that the ionic radii increase from titanium(IV) to hafnium(IV) (8,9). These complexes will be investigated under inert conditions by use of nuclear magnetic resonance, vibrational spectra, and x-ray powder diffraction and GC/Mass Spectrometry. It is aimed to elucidate the structure and to ascertain the mode of bonding in the products obtained by the reactions of the metal halides and oxyhalides with potassium dihydrobis(pyrazolyl)borate, potassium hydrotris(pyrazolyl)borate, and potassium tetrakis(pyrazolyl)borate.

References

1. Vilk, W.; Stotler, H.H., Journal of Metals, 1970, 22, 50.
2. Chase, J.D.; Skrivan, J.F., AlChE Symposium Series, 1979, 75, 38.
3. McLaughlin, W.J., "Plasma Reduction of Titanium Dioxide," U.S. Patent 3,429,691, 1969.
4. Asslani, S.S.; Rahbornochi, R.; Wilson, B., Inorg. Chem. Lett., 15, 59 (1959)
5. Trofimenko, S., J. Amer. Chem. Soc., 1966, 88, 1842.
6. Trofimenko, S., J. Amer. Chem. Soc., 1967, 890, 3270.
7. Trofimenko, S. Chem. Rev., 1972, 72, 497.
8. Calderon, J.L.; Cotton, F.A.,; Shaver, A., J. Organometal. Chem., 1972, 37, 127.
9. Bagnell, K.W.; Edwards, J.; Preez, J.G.H.; Warren, T.F., J. Chem Soc. (Dalton), 1975, 140.